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# The continuing drama of the half-metal/semiconductor interface

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**Abstract**
In this article, based on electronic structure calculations, the conditions are discussed under which a genuine half-metallic interface between a heusler $C1_b$ half-metal and a semiconductor can exist. An explanation is given why for the III–V semiconductors the double anion terminated (111) interface is the only possible interface. For semiconductors, based on transition metals, a much wider variety of interfaces are found to be possible.

## 1. Introduction

Nowadays it is generally accepted that the physical and chemical properties of surfaces are in general quite distinct from the corresponding properties in the bulk of a material. This is the rule for a vast majority of materials, although the details of the surface properties depend on the electrical behaviour of the bulk. The majority of metals are pyrophoric, including common metals like iron and aluminium. They owe their stability to protective, chemically inert surface layers. Surfaces of metals are actively studied, experimentally as well as computationally. Surface reconstructions have been an active area of research for decades in the field of semiconductors. The applications of III–V semiconductors in microelectronics have been slowed down considerably, in part because of the unfavourable surface properties as compared with silicon based devices.

The interest in surfaces of half-metals is more recent. Activities were triggered by the difficulty of extracting 100% spin-polarized electrons from half-metals (Bona *et al* 1985), whose bulk half-metallic properties themselves are not in doubt (Hanssen *et al* 1990). Consequently, most studies have concentrated on the question of whether the half-metallic properties extend to the surface, to understand a possible failure to do so and the design of a possible cure. The differences between surface and bulk properties in half-metals are dependent on the origin of the half-metallicity itself. Strongly magnetic half-metals, like the colossal-magneto resistance materials and for example chromium-dioxide, behave distinctly from heusler alloys, in particular the ones in the $C1_b$ structure. In the former ones, the half-metallic properties are practically determined by the species carrying the magnetic moment alone (i.e. the manganese in the CMR materials or the chromium in $CrO_2$). As long as the valences of these ions are maintained at the surface, the half-metallic properties prevail. For example, the density of states of the alkaline-earth- oxygen terminated (001) surface of $LaSr_2Mn_2O_7$ is remarkably similar to the density of states in the bulk (de Boer and de Groot 1999), with the fermi-energy at the top of the valence band. The electronic structure of the stoichiometric (001) surface of chromium-dioxide shows two oxygen derived surface states in the lower part of the band-gap, but they are at a comfortable distance from the fermi-energy, which is located in the middle of the gap here (van Leuken and de Groot 1995). Chromium-dioxide shows the highest spin-polarization at the surface of all half-metals (Ji *et al* 2001). Actually it is the only half-metal, where all measurements at the surface show the complete spin polarization expected of half-metals. The two cases mentioned here have relatively simple surfaces, since they are electrically neutral already without surface reconstructions, segregations, etc. However it is also expected that for more complex surfaces the half-metallic properties will be unaltered at the surface as long as the valence of the magnetic species is unaffected.

The situation in a half-heusler alloy like NiMnSb is fundamentally different. The half-metallic bandgap is similar to the bandgap in the III–V semiconductors: manganese is trivalent like gallium in GaSb; the antimony is pentavalent while the role of the nickel is to mediate the manganese–antimony interaction (de Groot *et al* 1983). It is vital that both the manganese and the antimony possess the tetrahedral coordination characteristic of the zinc-blende structure. In

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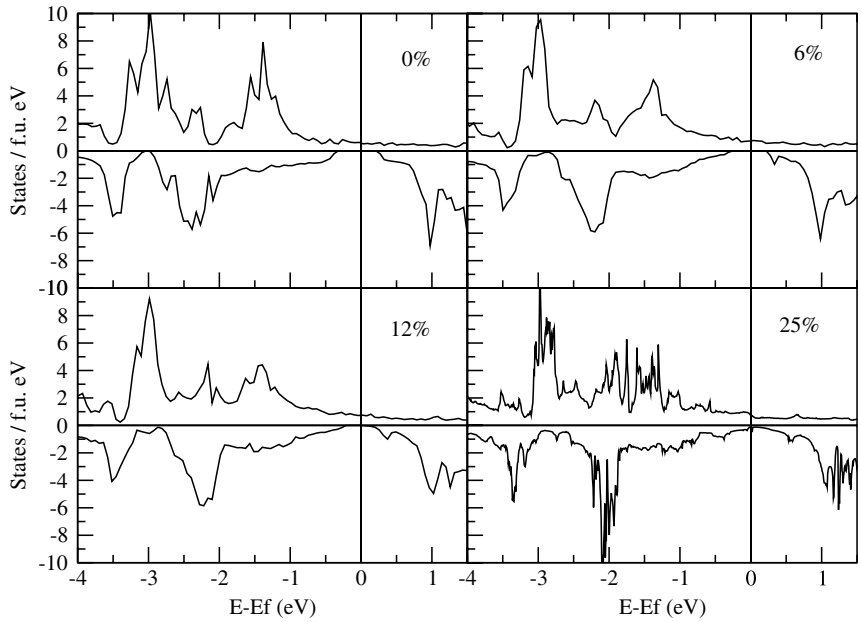


**Figure 1.** Density of states curves for $NiMn_{(1-x)}Ga_xSb$ close to the Fermi-energy for $x = 0$, $x = .06$, $x = .12$ and $x = .25$. In the latter case, the bandgap for the minority spin-direction has disappeared.

other words, the half-metallic properties in a half-metal like NiMnSb are not only dependent on the right elements and valences but also depend sensitively on the crystal structure. This is the reason why weakly magnetic half-metals like the heuslers will in general not posses half-metallic surfaces, where as strongly magnetic half-metals like chromium-dioxide do. The degree of spin-polarization of the various surfaces, of for example NiMnSb, varies as a function of the orientation and the composition. It can be fairly high: however, genuine half-metallic magnetism is absent for all surfaces studied (Jenkins and King 2001) (de Wijs and de Groot 2001) (Galanakis 2002) (Jenkins 2004). This looks like a bad starting point for the construction of a half-metallic *interface.*

In most cases such an interface will be with a semiconductor and sometimes with a metal. The interface with a semiconductor will often have the injection of spin-polarized charge carriers as the goal. As a result of the conductivity mismatch between (half) metal and semiconductor (Schmidt *et al* 2000), a genuine half-metallic interface is desirable, i.e. a situation where for one spin-direction nowhere metallic conduction is possible: not in the half-metal, not in the interface nor in the semiconductor.

The use of heusler alloys may not be as bad as the lack of half-metallicity at their surfaces suggests: *if* the semiconductor under consideration is a III–V semiconductor, the similarity in electronic structure with NiMnSb may restore the half-metallicity at the interface, which was lost at the surface. Vacuum at a heusler surface is simply much more detrimental than a semiconductor. On the other hand, the use of an oxidic half-metal at an interface with a zinc-blende semiconductor may very well induce metallic states for the minority (semiconducting) spin-direction in the *semiconductor*.

Genuine half-metallic interfaces of NiMnSb with InP and CdS were obtained in the (111) direction with both half-metal and semiconductor being anion terminated at the interface (de Wijs and de Groot 2001). This is the only interface showing genuine half-metallicity, but the detailed origin of the unique properties of this interface has never been explained. This is the subject of the first part of this paper. The second part uses the conclusions of the first part and attempts to select semiconductors that show genuinely half-metallic interfaces for more than one and preferably all orientations of the interface.

## 2. Genuine half-metallic interfaces: zinc-blende semiconductors

In the introduction the importance of the similarity between the electronic structure of the minority spin-direction of NiMnSb and III–V semiconductors was stressed. But there are also differences, however. One of these differences has been discussed in the literature: where the metal states important for the band-gap formation are *even* in the half-metal (manganese d-states) and *odd* for the III–V semiconductor (for example Ga p states). This difference is unimportant as long as the crystal structure does not possess inversion-symmetry. But this difference is the origin of the different electronic structures of half- and full-heuslers since the latter do possess inversion-symmetry. Another difference is of importance for interfaces between NiMnSb and III–V semiconductors. The relevant states for the anion are identical, of course. But where the relevant states for the III–V semiconductor have the same principal-quantum number (for example 4s and 4p for gallium), they are different in the half-metal (4s and3d). This means that the ordering in energy between the s function and the other function is reversed. The influence of this difference can be seen in figure 1. The substitution of manganese by gallium leads to the introduction of gallium impurity s states where these s states are found in the III–V semiconductor: at the bottom of both valence and conduction-band. Already at concentrations lower than those expected at the interface,

the bandgap has disappeared. In other words, the semiconducting properties can be obtained equally well with a transition-metal (the half-metal) or a main-group-metal (the III–V semiconductor) but *not with a mixture of them.* Note that this situation is not unrelated the limited substitution range of transition metals in III–V semiconductors as experienced in magnetic semiconductors.

Let us consider the interfaces of low index. The 100 planes in NiMnSb consist of alternate layers containing Ni and Mn,Sb. The 110 planes contain all three components, while the 111 planes contain just one component each in the order Mn, Ni, Sb . The genuine half-metallic interface reported thus far is the 111 interface with anion termination for both half-metal and semiconductor at the interface. It is clear now why this is so: it is the only interface *without anions coordinated by a mixture of main-group- and transition-metals.* The anion–anion bond at the interface is not unusual; it occurs also in several minerals like gudmundite, costibite and paracostibite (de Wijs and de Groot 2001).

## 3. Genuine half-metallic interfaces for more orientations

In many cases, the choice of the semiconductor will be based on a specific application. If there is some freedom in the choice of the semiconductor, one could use this in order to select a semiconductor imposing less stringent requirements on the interface as compared with a traditional III–V semiconductor. In view of the lessons from the previous paragraph, semiconductors based on transition-metals rather than main-group-metals should be considered. Also similarities in crystal structure and minimal lattice mismatch are points of consideration. For these reasons we limit ourselves to non-magnetic semiconductors in the heusler $C1_b$ structure. The magnetic moment of NiMnSb is $4\,\mu$b; hence a reduction of the number of electrons by this number will either lead to a half-metallic antiferromagnet or a non-magnetic semiconductor. Replacement of Mn by Sc leads to the existing compound NiScSb, which crystallizes in the heusler $C1_b$ structure indeed (Pecharskii *et al* 1983). Two isoelectronic, existing alloys are also of importance: NiTiSn (Jeitschko 1970) and CoTiSb (Szutula *et al* 1973). All three compounds are non-magnetic semiconductors. The electronic structure, the magnetic and electrical properties of the latter two were studied by Tobola *et al* (Tobola *et al* 1998). Figure 2 shows the bandstructure of NiScSb. It is a semiconductor with an indirect bandgap; the bottom of the conduction band is located at the X point, just as in CoTiSb. Table 1 compares lattice parameters, lattice mismatch and bandgaps with NiMnSb. The three semiconductors have advantages and disadvantages in combination with NiMnSb. NiTiSn has a very small lattice mismatch with NiMnSb (.2%) and a good match in bandgap as well. (It should be realized that the bandgaps for the semiconductors are underestimated in the calculations. This is *probably* not the case for half-metals.) CoTiSb on the other hand has a larger bandgap, which may be advantageous in some cases. The lattice mismatch is somewhat larger. NiScSb has an even larger mismatch, but it has the advantage of introducing one new element only, thus minimizing complications related to interdiffusion. Another advantage of NiScSb is that it shows

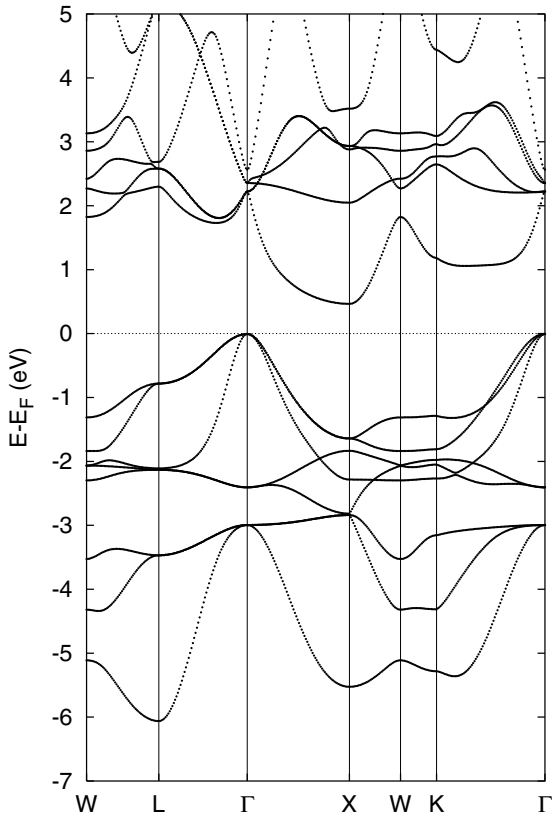


**Figure 2.** Bandstructure of the non-magnetic semiconductor NiScSb.

**Table 1.** Calculated bandgap, lattice parameter and lattice mismatch with respect to NiMnSb for several semi-conducting heusler compounds.

| Compound | Bandgap (eV) | Lattice parameter (pm) | Lattice mismatch (%) |
|---|---|---|---|
| NiMnSb | .63 | 592.9 | - |
| NiScSb | .47 | 605.5 | 2.1 |
| NiTiSn | .45 | 594.1 | 0.2 |
| CoTiSb | .95 | 597.9 | 0.8 |

genuine half-metallic interfaces with NiMnSb for *all* interfaces of low index (Attema *et al* 2004).

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